(54) Title: RADIATION CURABLE RESINS COMPRISING HYPERBRANCHED POLYESTERS

(57) Abstract

Hyperbranched polyester of a polyol with 3 to 10 reactive hydroxyl groups, preferably of equivalent reactivity, and an aromatic polycarboxylic anhydride with 2 to 4 carboxyl groups, preferably 3 carboxyl groups, each hydroxyl group of the polyol forming an ester linkage with one anhydride group of the polycarboxylic anhydride, and further glycidyl (meth)acrylate or allyl glycidyl ether forming ester linkages with the remaining carboxyl groups of the anhydride and free hydroxyl groups. Further in the hyperbranched polyester (meth)acrylic anhydride and/or an aliphatic carboxylic anhydride form ester linkages with the free hydroxyl groups. The invention also comprises a process for the production of hyperbranched polyesters and such polyesters obtainable by the process. The hyperbranched polyesters can be used as resins, curable by UV irradiation, for the production of coatings, adhesives, laminates, foils and thin films and fibre-reinforced composites.

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Radiation curable resins comprising hyperbranched polyesters

The present invention relates to new hyperbranched polyesters and a process for the production thereof and curable resins comprising the polyesters.

5   Radiation-curable resins are increasingly used in various industrial applications, replacing conventional thermally cured and solvent based coatings and adhesives. The radiation-curable resins have favourable properties, e.g., high speed and low energy consumption of cure, solvent-free
10   formulations, room temperature operation and high quality end-products. The principal components of a radiation-curable resin are oligomers (or prepolymers) and comonomers. The oligomers constitute the backbone of the three-dimensional polymer network formed by curing. Important types of oligo-
15   mers commonly used for coating are acrylated epoxies, acryla- ted polyurethanes, unsaturated polyesters and acrylated polyesters (or polyethers) which give desired properties of the final cured films. However, those oligomers usually consist of linear molecular chains. The viscosity of the
20   resin increases rapidly with increasing chain length of the oligomer. To obtain an operational viscosity of the formula for spraying, dipping, roll coating, etc., large amounts of multifunctional comonomer are required for the primary func- tion of viscosity control. In addition, the comonomers have
25   important effects on the cure reaction and the properties of the final product. Some of the comonomers have low cure rate, cause shrinkage of the film during curing, and have high costs and a limited shelf life. Multifunctional acrylates are the preferred monomers in radiation-curable systems because
30   of their rapid curing rates and low prices. The common acrylate monomers are volatile and toxic, and have strong odour. Therefore, the trend is to use radiation-curable oligomers with viscosity close to the required application viscosity in order to reduce or eliminate the use of comono-
35   mers.

          An object of the present invention therefore was to obtain oligomers with reduced viscosity compared to known

oligomers with similar molecular weight.

A further object of the invention was to present oligomers which in resin applications needs a lower amount of multifunctional comonomers or none at all, while the resins

5   still have a low viscosity, a high cure rate, an acceptable degree of curing and the final products have good mechanical properties.

A further object of the invention was to offer a process for the production of such oligomers.

10   The objects of the invention was solved by the hyperbranched polyester, the process for the production of these hyperbranched polyesters and resin comprising them, as claimed in the claims.

Oligomers with a strongly branched structure are a

15   new family of polymers which has been attracting increasing interest for many applications, e.g., in agriculture, medicine, cosmetics, adhesives and coatings. The oligomers are referred to as hyperbranched polyesters with a three-dimensional molecular architecture and possessing starburst

20   topology (D.A. O'Sullivan, Chem. Eng. News, 20 (1993); D.A. Tomalia, A.M. Naylor, and W.A. Goddard III, Angew.Chem. Int. Ed.Engl., 29, 138 (1990). An important structural difference between linear oligomers and hyperbranched polyesters is that a linear oligomer of sufficient molecular weight contains an

25   entanglement of flexible molecular chains, while a hyperbranched polyester is a compact molecule with many branches which carry a high number of terminal functional groups on each molecule.

With the present invention it was found that hyper-

30   branched polyesters with reactive acrylate double bonds at chain extremities can be used to reduce viscosity, increase reaction rate, and improve adhesion to substrates due to their very special molecular structures. This new kind of molecules modifies the physical and chemical properties both

35   of the resin system and of the final product after curing, thereby facilitating their use in coating and adhesive systems. Further, with the present invention hyperbranched

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polyesters with high molecular weight can be obtained in a
simple process from readily available and inexpensive raw
materials.

Hyperbranched polyester research is still fairly
new, and to date no commercial products are available. The
main difficulties in preparing three-dimensional and ordered
hyperbranched polyesters are preserving the regularity and
order in the structures, characterization of the products,
and separating the products from the excess of reactants.
Little work has been performed to prepare adhesive and coat-
ing systems with hyperbranched polyesters, especially for
radiation curing applications. A series of work on allyl
ether maleate hyperbranched polyesters for UV curing coatings
have been reported (M.Johansson, E. Malmström, and A.Hult,
J.Polym.Sci., Part A: Polym.Chem., 31, 619 (1993); E.Malm-
ström and A.Hult "Hyperbranched polyesters and their Degree
of Branching as Determined by ^{13}C-NMR", Proceedings of Nordic
Polymer Days 1994.).

With the present invention it has been possible to
synthesize a series of new hyperbranched (meth)acrylated
polyesters with different number of terminal double bonds per
molecule. The rheological properties of the resins prepared
from the polyesters and the mechanical properties of UV cured
films are improved in a pronounced manner compared with known
polymers.

Thus, the present invention relates to a hyperbran-
ched polyester of a polyol with 3 to 10 reactive hydroxyl
groups, preferably of equivalent reactivity, and an aromatic
polycarboxylic anhydride with 2 to 4 carboxyl groups, prefer-
ably with 3 carboxyl groups,

each hydroxyl group of the polyol forming an ester
linkage with one anhydride group of the polycarboxylic
anhydride,

and further glycidyl (meth)acrylate or allyl glyci-
dyl ether forming ester linkages with the remaining carboxyl
groups of the anhydride and free hydroxyl groups.

The invention further relates to a hyperbranched

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polyester as defined above in which (meth)acrylic anhydride
and/or an aliphatic carboxylic anhydride form/s ester link-
ages with the free hydroxyl groups.

The present invention further relates to a process
5   for the production of a hyperbranched polyester, and hyper-
branched polyester obtainable by the process characterized in
that it comprises the following steps:
a) reacting an aromatic polycarboxylic anhydride with 2 to 4
carboxyl groups, preferably 3 carboxyl groups, with a polyol
10 with 3 to 10 reactive hydroxyl groups, preferably of equival-
ent reactivity, in the presence of an activating agent, the
amount of anhydride being at least one mole of anhydride per
hydroxyl group in the polyol,
b) reacting the product from a) with glycidyl (meth)acrylate
15 or allyl glycidyl ether in an amount at least corresponding
to one mole of glycidyl (meth)acrylate or allyl glycidyl
ether per free carboxylic acid group of the product of a).
The process and the polyester obtainable by the process can
further comprise the following step:
20 c) the product from step b) is further reacted with (meth)-
acrylic anhydride in an amount sufficient to esterify a part
or all of the free hydroxyl groups of the product from step
b). The products from step b) or c) can further be reacted
with an aliphatic carboxylic anhydride in an amount to
25 esterify a part of or all of the remaining hydroxyl groups of
the products.

Two principally different methods have been devel-
oped for the synthesis of hyperbranched polymers: a conver-
gent growth approach, where growth begins at the chain ends,
30 and a divergent growth approach, where growth begins at a
central core. In the present invention, the hyperbranched
polyesters with terminal double bonds were synthesized by
controlled stepwise divergent preparation, i.e., the syn-
thesis started at the centre of the hyperbranched polyester.
35 Two or three steps were needed to obtain hyperbranched
polyesters with a predetermined number of terminal double
bonds located at the surface of the oligomeric sphere. The

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reaction scheme for the synthesis of the hyperbranched
polyester can be illustrated for a polyol with 4 hydroxyl
groups as shown in Figure 1 (B is hydroxyl groups, and D is
unsaturated groups). New nomenclature developed by K. L.
Wooley, J. M. J. Fréchet and C. J. Hawker, Polymer vol. 35,
No. 21, 1994, names the starburst hyperbranched molecule of
Figure 1 a dendritic polymer.

In the first reaction step an aromatic carboxylic
anhydride with 2 to 4 carboxyl groups, preferably 3 carboxyl
groups, and a polyol with 3 to 10 hydroxyl groups and an
activating agent were heated to temperatures about or below
100°C, preferably initially to 70 to 80°C and gradually
increasing to about 100°C at the end of the reaction, in the
presence of a solvent and under inert gas atmosphere, prefer-
ably nitrogen atmosphere. The aromatic carboxylic anhydride
is most preferably 1,2,4-benzenetricarboxylic anhydride.
Suitable polyols are all polyols having 3 to 10 hydroxyl
groups and the hydroxyl groups are preferably of equivalent
reactivity, which means that the esterification of each
hydroxyl group will proceed equally easy to start the build-
ing up of the regular molecule. Examples of such polyols are
trimethylolpropane, pentaerythritol or a dimer thereof, mono-
and disaccharides, with pentaerythritol as a preferred embod-
iment. The amount of added anhydride is at least one mole of
anhydride per hydroxyl group of the polyol, but preferably
the anhydride is added in an excess amount. An excess of 20 -
50 mol % is suitable. An activating agent is used to activate
the anhydride group. The activating agent is present in a
catalytic amount. As activating agent stannous chloride is a
preferred embodiment. A suitable solvent is for example N,N-
dimethylformamide (DMF).

For a product mixture of 1,2,4-benzenetricarboxylic
anhydride with pentaerythritol the IR spectrum with residual
1,2,4-benzenetricarboxylic anhydride is shown by curve 1 in
Figure 2. Toluene was used to wash the reaction product to
remove the excess of 1,2,4-benzenetricarboxylic anhydride
until no peaks at 1760 and 1850 cm^{-1} for anhydride groups

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could be observed, shown as curve 2 in Figure 2. The wide
absorption bands at the range of 2750 to 3400 cm^{-1} in the IR
spectrum indicate the terminal carboxyl groups on the benzene
ring. For this product mixture each polyolester of the poly-

5   carboxylic acid anhydride has two carboxyl end groups. Three
isomer products could be obtained in this system, and the
molecular structures are shown in Figure 3. The product is
largely a mixture of meta and para isomers of the ester
according to the relative reactivity of the anhydride and the

10   carboxyl groups at low reaction temperature. A small amount
of ortho isomer is expected to be a hydrolysis and reesteri-
fication product of para and meta polyolester formed. The
reaction of carboxyl and hydroxyl groups is favoured at
elevated temperatures.

15   The polyolester was further reacted with glycidyl
(meth)acrylate or allyl glycidyl ether in an amount at least
corresponding to one mole of glycidyl (meth)acrylate or allyl
glycidyl ether per free carboxylic acid group of the formed
polyester, preferably in an excess amount, i.e. about 5 wt%.

20   Glycidyl acrylate is the preferred reactant. The reaction is
carried out in a solvent, such as a mixture of DMF and
toluene in the presences of a basic catalyst and an inhibitor
for radical polymerization until no carboxyl groups could be
detected by end-group titration. As basic catalysts common

25   bases can be used, but benzyl dimethyl amine is preferred.
Conventional inhibitors such as hydroquinone is used. The
reaction temperature is below 100°C, preferably about 70°C.
The IR spectrum of the product is shown as curve 3 in Figure
2. The appearance of the wide absorption at around 3460 cm^{-1}

30   means the formation of hydroxyl groups on the molecular
chains due to reaction of epoxy and carboxyl groups. Finally,
residual solvent was removed by evacuation at low tempera-
ture. The final "starburst" hyperbranched polyester products
with double bonds at the end groups are translucent viscous

35   liquids with one hydroxyl group at each end group. The mol-
ecular structure, when started with pentaerythritol, is
ideally sphere-like, with about 8 end-double bonds. The

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principal formula is shown in Figure 4.

The hydroxyl groups of the hyperbranched polyester
with terminal double bonds were reacted further by ester
formation with (meth)acrylic anhydride in an amount suffi-
5 cient to esterify a part of or all of the free hydroxyl
groups in order to prepare the hyperbranched polyester mol-
ecules with further end-double bonds. Of the two acrylic
anhydrides, the methacrylic anhydride is preferred. The
hyperbranched polyester started from pentaerythritol with
10 about 16 end-double bonds with the idealized formula is shown
in Figure 5. The IR spectrum of the hyperbranched polyester
with about 16 double bonds is shown by curve 4 in Figure 2.
Almost no peak for hydroxyl group could be observed.

In a last step the product with end-double bonds is
15 reacted with an aliphatic carboxylic anhydride, preferably
acetic anhydride to esterify a part of or all of the remain-
ing hydroxyl groups on the molecular chains for decreasing
molecular polarity of the hyperbranched polyester, and im-
proving its compatibility with multifunctional comonomers.
20 This esterification can also be made of the hydroxyl groups
of the hyperbranched polyester before the previous reaction
with (meth)acrylic anhydride, thus omitting the further
introduction of (meth)acrylic double bonds. The final hyper-
branched polyester products with terminal double bonds after
25 modifying, prepared in the present invention are fairly
transparent colourless viscous liquids. As shown in Figure 4
and 5 the double bonds are in end groups, located at the
surface of the oligomeric sphere, which is highly favourable
for UV cure.

30   The polydispersity measured by GPC analysis (Figure
6) varied from 1,4 to 1,9 at different reactant ratios and
reaction temperatures with molecular weights of maximum 2500
obtained, which corresponds to a modified polyester molecule
with four main branches. The wide molecular weight distribu-
35 tion is mainly attributed to incomplete reaction between
1,2,4-benzenetricarboxylic anhydride and pentaerythritol,
hyperbranched polyester fragmentation during hyperbranched

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polyester growth, and to the small excess of glycidyl
(meth)acrylate monomer which react further with by-products
in the system, responsive to UV irradiation.

5   The hyperbranched polyester according to the inven-
tion can be used as curable resins. The resins are preferably
cured by UV or EB radiation and most preferably by UV radi-
ation. The resins have lower viscosity than known oligomer
resins and can be used without a comonomer or with lower
amounts of comonomer than for conventional oligomer resins.

10   The UV curing of the resin according to the invention is very
rapid, down to parts of a second at room temperatur oper-
ation. This means a high speed of cure and low energi con-
sumption. The obtained products have a high glass transition
temperature, resulting in products of high hardness, for

15   example coatings or laminates with high surface hardness.

          The resins are solvent free and can be prepared
from 100 % of the hyperbranched polyester according to the
invention. The resins can however, also comprise multifunc-
tional monomers. A suitable amount of comonomer is 5 - 20 wt

20   % and the rest 80 - 95 wt % being the hyberbranched
polyester. The resins preferably comprise a photofragmenting
initiator. The amount of photofragmenting initiator used is
in the range 1 - 5 wt % based on the resin. Conventional
photofragmenting initiators can be used and a preferred

25   initiator is benzoyl dimethylketol. As multifunctional mono-
mers compounds with reactive double bonds can be used, such
as trimethylolpropane tri(meth)acrylate, hexandiol diacryla-
te, trimethylolpropane triallylether, pentaerythritol tri/te-
tra-allylether, triallylcyanurate, trimethylolpropane tri-

30   acrylether, pentaerythritol tetraacrylether. Trimethylolpro-
pane triacrylate being a preferred embodiment.

          The resin according to the invention can be used in
many different fields of which could be mentioned coatings,
adhesives, laminates, foils and thin films and fibre-rein-

35   forced composites.

          The invention will now be illustrated with
the following examples which however, are not intended to

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restrict the invention. With parts and per cent are meant
parts per weight and weight-%, if nothing else is mentioned.

The following chemicals are used:

5   Pentaerythritol [PETL]

    1,2,4-Benzenetricarboxylic Anhydride [BTCA]

    Glycidyl Acrylate [GA]

    Methacrylic Anhydride [MAA]

    Acetic Anhydride [AA]

10 Stannous Chloride [SC]

    Benzyldimethylamine [BDMA]

    Hydroquinone [HQ]

    Dimethyl Formamide [DMF]

    Trimethylolpropane Triacrylate (TMPTA)

15 Benzoyldimethylketol (BDK)

Example 1

        92,2 g (0.48 mol) BTCA is dissolved in 100 ml DMF
    at 80°C. 10.9 g (0.08 mol) PETL and 0.1 g (0.1 wt%) SC are
20 added, and the solution is kept at 80°C for 8 hours, and then
    heated to 100°C for 10 hours under N_2. Most of DMF is
    distilled off in vacuum and toluene is poured into the prod-
    uct to dissolve the residual BTCA. The product is washed with
    toluene until no BTCA is detected in IR spectra (1760 and
25 1850 cm^{-1} for anhydride groups). 57.2 g polyolester is
    obtained, as a white powder, with the yield of about 79 %
    after completely removing the solvents. The acid number of
    475 mg KOH/g polyester is determined by titration with 0.1 N
    KOH. 65.09 g (0.508 mol with a 5 % excess) GA is added slowly
30 drop by drop at 70°C together with 5 g (2.5 %) BDMA as cata-
    lyst and 1000 ppm HQ as inhibitor, dissolved in 70 ml DMF.
    After 7 hours at 70°C no carboxyl groups can be detected by
    titration. DMF is distilled off in vacuum. The product is a
    viscous liquid with maximum 8 acrylate and 8 hydroxyl groups
35 per molecule. This product is called D-1OH.
        12.4 g (0.121 mol) AA is added to 40.8 g D-1OH in
    50 ml DMF which reacts with about 6 hydroxyl groups per

molecule (averaged about 2 OH groups per molecule remain).
The product solution is then heated for 2 hours at 70°C and
DMF is distilled off in vacuum. The obtained product, called
D-1, is a viscous liquid with about 8 acrylate groups and 2
5   hydroxyl groups per molecule.

Example 2

40.8 g D-1OH is dissolved in 50 ml DMF with 500 ppm
HQ and 12.4 g (0.08 mol) MAA and 4.1 g (0.04 mol) AA are
10   added slowly, drop by drop at 70°C for two hours to react
with the hydroxyl groups. DMF is removed by vacuum distilla-
tion. The product, called D-2, is a viscous liquid with about
12 (meth)acrylate groups and 2 hydroxyl groups per molecule.

15   Example 3

40.8 g D-1OH is dissolved in 50 ml DMF with 500 ppm
HQ as inhibitor. 24.8 g MAA (0.161 mol) is added and heated
to 70°C. After 2 hours the reaction is complete. DMF is
removed by vacuum distillation. The product, called D-3, is a
20   viscous liquid with about 8 acrylate and 8 methacrylate
groups per molecule.

The dynamic viscosity for the products from
Examples 1 to 3 was measured as a function of frequency for
the hyperbranched polyesters with different numbers of double
25   bonds, as shown in Figure 7. The hyperbranched polyester D-1-
OH, according to Example 1, with about 8 double bonds and
without acetic anhydride modification, has the highest vis-
cosity due to the many hydroxyl groups in the system, resul-
ting in intermolecular hydrogen bonding (hyperbranched
30   polyester aggregation). At decreasing hydroxy functionality,
the dynamic viscosities of the hyperbranched polyester large-
ly decrease in order of D-1, D-2 and D-3, according to
Examples 1 to 3, at lower frequency. D-3 has the lowest
viscosity compared with D-1 and D-2 because of the high
35   number of double bonds (no remaining hydroxyl groups) at the
surface of the spherical molecule. This results in increasing
symmetry of the hyperbranched molecule, apart from less

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influence from the hydrogen bonding.

Low viscosity is particularly important in control-
ling the levelling time of a coating and for evaluation of
the processability of a radiation curable coating and adhes-
5   ive. This is especially the case for 100% solid coating
systems for thin films. The oligomer is the principal consti-
tuent and primarily responsible for the basic properties of
the coating. The viscosity of the oligomer is, therefore, an
important parameter since it determines the amount of
10   oligomer required in the final product. For control of the
viscosity of the radiation curable resin there are only two
parameters, namely the viscosity of the oligomer and the
amount of comonomer added.

The principal rheological difference between the
15   branched and the linear polyester molecules lies in the
smaller spatial extension of the branched molecule at a given
molecular mass. The viscosity of the resin is related to the
dynamic extension in space and the segment density within the
volume of the molecule. Therefore, the sphere-like starburst
20   (meth)acrylated polyester according to the invention has
lower viscosity than the linear polyester.

Flow time measurements are another evaluation of
the relative viscosity of various coatings and adhesives,
using a viscosimetric cup. The viscosities of the hyperbran-
25   ched (meth)acrylated polyesters containing 15 wt% tri-
methylolpropane triacrylate (TMPTA), as comonomer and a
conventional epoxy acrylate modified unsaturated polyester
(MUP) containing 35 wt% TMPTA at 21°C are compared in Figure
8. It can be seen that the flow times through the viscosimet-
30   ric cup for hyperbranched polyester resins are much shorter
than for MUP resin. This means that the viscosity of MUP is
much higher than that of hyperbranched polyester. A practical
consequence is that the processability of hyperbranched
polyester containing resins is improved due to lower viscos-
35   ity.

Example 4:

3 parts of BDK were dissolved in 100 parts of a

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mixture of 15 % by weight of TMPTA and 85 % by weight of D-1,
D-2 or D-3, the resultant resins were coated on a
polyethylene terephtalate (PET) sheet. The test samples were
cured in air on a conveyer belt with variable speed by UV
5   irradiation for 0.15 seconds under a 300 W/in (120 W/cm)
Model F300 D bulb (Fusion UV Curing Systems) in the exposure
chamber.

Example 5:

10   The procedure of Example 4 was repeated except that
100 parts of D-1, D-2 or D-3 polyesters are used instead of
the mixture of the polyesters and TMPTA.
         The irradiation time is varied by changing the
speed of the conveyor belt. The polymerization rate of the
15   hyperbranched polyester resins was determined by measuring
the irradiation time required to obtain fully tack-free state
for the cured film using a cotton bar. The data are given in
Figure 9. The resin with oligomer D-3 needs the shortest
curing time to get tack-free state.
20   The glass transition temperatures of the crosslin-
ked (meth)acrylated hyperbranched polyesters D-1, D-2 and D-3
according to Example 5 from Dynamic Mechanical Thermal Analy-
sis (DMTA) measurements are given in Figure 10. It can be
seen that the glass transition temperature increases rapidly
25   with increasing functionality of the cured hyperbranched
oligomer.
         The physical properties of the cured material are
related to the structure of the crosslinked network. The
glass transition temperature, T_g, is a function of the flexi-
30   bility of the polymeric chains. If the flexibility decreases,
the transition temperature increases. Flexibility is a func-
tion of chain structure, crosslinked structure and crosslink
density. For the hyperbranched polyesters the spherical shape
of the molecules and the high crosslink density due to its
35   high functionality decreases the flexibility of the cured
films. Therefore, crosslinked hyperbranched polyester give
higher glass transition temperature than crosslinked linear

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oligomers as an effect of the structural difference.

The measurements made in the present invention were performed accordingly:

Molecular Weight Distribution

5   Measurements of molecular weight distribution were performed on a WATERS 410 GPC system equipped with a WISP 712 automated injector. The columns used were μ-Styragel of pore sized: 500, 10^5, 10^4, 10^3, and 100 Ångström with polystyrene standards for calibration and tetrahydrofuran (THF) as sol-
10   vent.

Dynamic Mechanical Spectroscopy

The dynamic mechanical properties of the hyperbranched polyesters were measured by shear rheometry (Dynamic Analyser RDAII). Viscous liquid samples were examined at 25°C
15   using two parallel plates of 12.5 mm radius with 0.62 to 0.76 μm gap over a wide range of frequencies.

Flow Time

Flow time of the resins with multifunctional monomer added was measured using a viscometric cup of number 68
20   for comparison of the viscosity of the hyperbranched polyesters with that of modified linear unsaturated polyester.

IR spectra

Infra-red spectra of the polyesters at different
25   reaction stages were recorded on a Perkin-Elmer Model 1710 Fourier Transform Spectrometer prepared as pressed KBr solid disk or smeared as an acetone solution of the resin on a NaCl prism to form a thin film.

Thermomechanical analysis

30   Dynamic Mechanical Thermal Analyser (DMTA, Polymer Laboratories MK II) was used to measure glass transition temperature (T_g) at the range of 40 to 250°C and 1 Hz frequency of completely UV cured films without TMPTA added.

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Claims

1. Hyperbranched polyester of a polyol with 3 to 10
reactive hydroxyl groups, preferably of equivalent
reactivity, and an aromatic polycarboxylic anhydride with 2
5   to 4 carboxyl groups, preferably 3 carboxyl groups,

each hydroxyl group of the polyol forming an ester
linkage with one anhydride group of the polycarboxylic
anhydride,

and further glycidyl (meth)acrylate or allyl
10 glycidyl ether forming ester linkages with the remaining
carboxyl groups of the anhydride and free hydroxyl groups.

2. Hyperbranched polyester of a polyol with 3 to 10
reactive hydroxyl groups, preferably of equivalent
reactivity, and an aromatic polycarboxylic anhydride with 2
15 to 4 carboxyl groups, preferably 3 carboxyl groups,

each hydroxyl group of the polyol forming an ester
linkage with one anhydride group of the polycarboxylic
anhydride,

and glycidyl (meth)acrylate or allyl glycidyl ether
20 forming ester linkages with the remaining carboxyl groups of
the anhydride and free hydroxyl groups,

and further (meth)acrylic anhydride and/or an
aliphatic carboxylic anhydride forming ester linkages with
the free hydroxyl groups.

25   3. Hyperbranched polyester obtainable by a process
comprising the following steps:
a) reacting an aromatic polycarboxylic anhydride with 2 to 4
carboxyl groups, preferably 3 carboxyl groups, with a polyol
with 3 to 10 reactive hydroxyl groups, preferably of
30 equivalent reactivity, in the presence of an activating
agent, the amount of anhydride being at least one mole of
anhydride per hydroxyl group in the polyol,
b) reacting the product from a) with glycidyl (meth)acrylate
or allyl glycidyl ether in an amount at least corresponding
35 to one mole of glycidyl (meth)acrylate or allyl glycidyl
ether per free carboxylic acid group of the product of a).

4. Hyperbranched polyester according to claim 3,

characterized in that activating agent is present in a
catalytic amount.

5. Hyperbranched polyester according to claim 3,
characterized in that the activating agent is SnCl₂.

6. Hyperbranched polyester obtainable by a process
comprising the steps a) and b) of claim 3 and the further
step:
c) the product from step b) is further reacted with
(meth)acrylic anhydride in an amount sufficient to esterify a
part or all of the free hydroxyl groups of the product from
step b).

7. Hyperbranched polyester obtainable by a process
comprising the steps a) and b) of claim 3 or the steps a), b)
and c) from claim 6 and the further step that the product
from step b) or c) is further reacted with an aliphatic
carboxylic anhydride in an amount to esterify a part of or
all of the remaining hydroxyl groups of the products.

8. Hyperbranched polyester according to claims 2, 6
and 7, characterized in that the (meth)acrylic anhydride and
the aliphatic carboxylic anhydride forming ester linkages
with the free hydroxyl groups is methacrylic anhydride and
acetic anhydride.

9. Hyperbranched polyester according to any of
claims 1 to 8, characterized in that the polyol is
pentaerythritol and the aromatic polycarboxylic anhydride is
1,2,4-benzenetricarboxylic anhydride and the
glycidyl(meth)acrylate is glycidyl acrylate.

10. Hyperbranched polyester according to any of
claims 1 to 9, characterized in that the hyperbranched
polyester is a dendritic polyester or a crosslinked dendritic
polyester.

11. A process for the production of a hyperbranched
polyester, characterized in that it comprises the following
steps:
a) reacting an aromatic polycarboxylic anhydride with 2 to 4
carboxyl groups, preferably 3 carboxyl groups, with a polyol
with 3 to 10 reactive hydroxyl groups, preferably of

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equivalent reactivity, in the presence of an activating
agent, the amount of anhydride being at least one mole of
anhydride per hydroxyl group in the polyol,
b) reacting the product from a) with glycidyl (meth)acrylate
5   or allyl glycidyl ether in an amount at least corresponding
to one mole of glycidyl (meth)acrylate or allyl glycidyl
ether per free carboxylic acid group of the product of a).

        12. A process according to claim 11, characterized
in that the activating agent is present in a catalytic
10 amount.

        13. A process according to claim 11, characterized
in that the activating agent is SnCl₂.

        14. A process according to claim 11, characterized
in that in step a) the reaction mixture is heated to a
15 temperature below 100°C.

        15. A process according to claim 11, characterized
in that the amount of anhydride in step a) and of acrylate in
step b) are in excess of the stated amount.

        16. A process according to claim 11, characterized
20 in that the reaction of step b) is made in the presence of a
basic catalyst and an inhibitor for radical polymerization.

        17. A process according to claim 16, characterized
in that the basic catalyst is benzyldimethyldiamine.

        18. A process according to claim 11, characterized
25 in that it further comprises the following step:
c) the product from step b) is further reacted with
(meth)acrylic anhydride in an amount sufficient to esterify a
part or all of the free hydroxyl groups of the product from
step b).

30   19. A process according to claim 18, characterized
in that the anhydride is methacrylic anhydride.

        20. A process according to claims 11 or 18,
characterized in that the product from step b) or c) is
further reacted with an aliphatic carboxylic anhydride in an
35 amount to esterify a part of or all of the remaining hydroxyl
groups of the products.

        21. A process according to claim 20, characterized

in that the aliphatic carboxylic anhydride is acetic
anhydride.

    22. A process according to any of claims 11 to 21,
characterized in that the polyol is pentaerythritol and the
5   aromatic polycarboxylic anhydride is 1,2,4-benzene-
tricarboxylic anhydride and the glycidyl(meth)acrylate is
glycidyl acrylate.

    23. A process according to any of claims 11 to 22,
characterized in that the hyperbranched polyester is a
10 dendritic polyester or a crosslinked dendritic polyester.

    24. A curable resin characterized in that it
comprises a hyperbranched polyester as defined in any of
claims 1 to 10.

    25. A curable resin according to claim 24,
15 characterized in that it further comprises a photofragmenting
initiator.

    26. A curable resin according to claim 24 or 25,
characterized in that it comprises a multifunctional monomer.

    27. A curable resin according to claim 26
20 characterized in that the multifunctional monomer is
trimethylolpropane triacrylate.

    28. A curable resin according to any of claims 24
to 27, characterized in that it is curable with UV
irradiation.

25   29. Use of a curable resin according to any of
claims 24 to 28 for the production of coatings, adhesives,
laminates, foils and thin films and fibre-reinforced
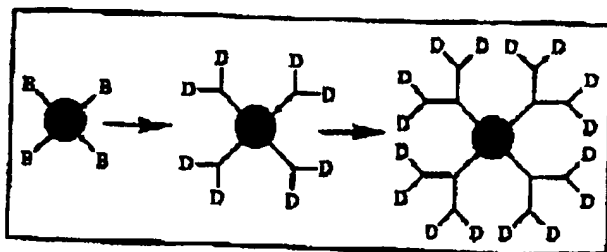composites.

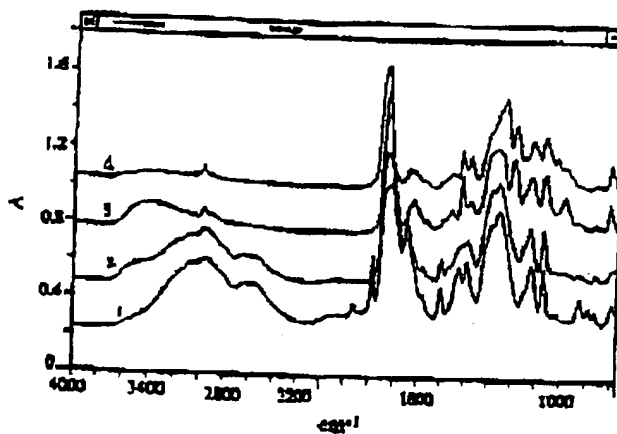Figure 1 Reaction scheme for the synthesis of the hyperbranched polyester.

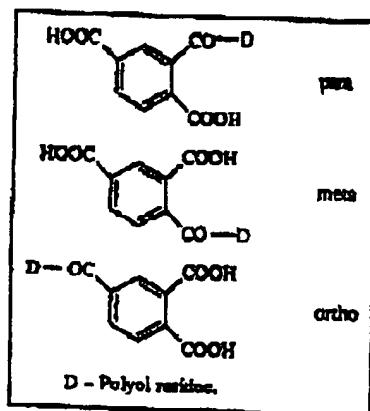Figure 2 IR spectra of the products at different reaction stages.

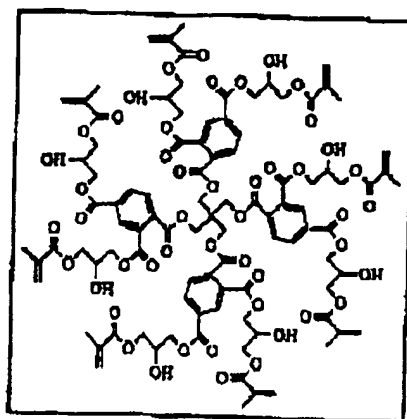Figure 3 Molecular structure of the three polyolester isomers.

Figure 4 Idealized formula of the hyperbranched methacrylated
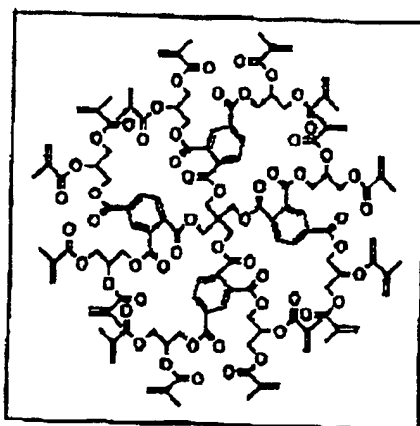polyester with 8 double bonds.

Figure 5 Idealized formula of the hyperbranched methacrylated
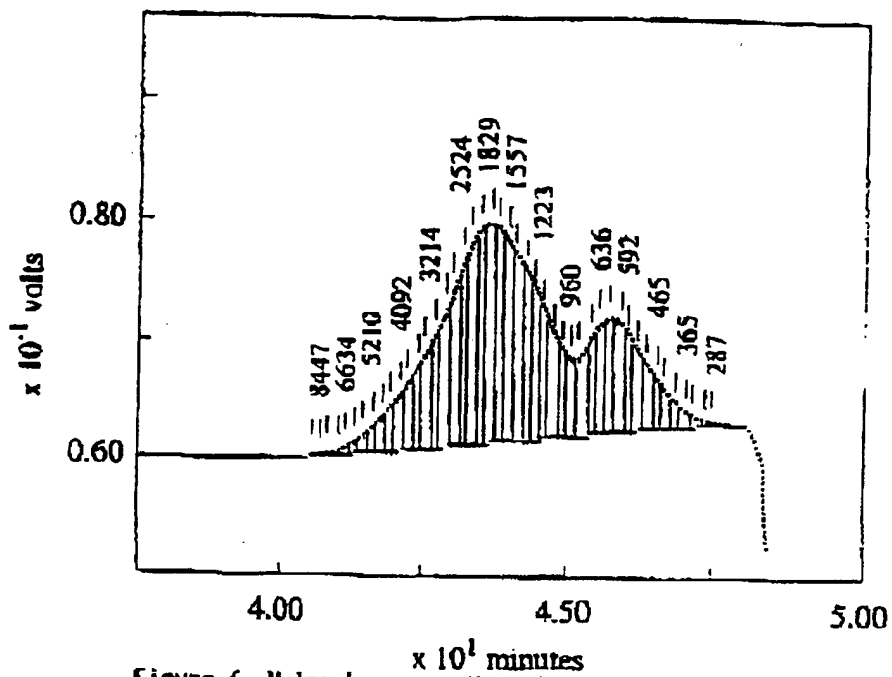polyester with 16 double bonds.

Figure 6   Molecular mass distribution of the hyperbranched methacrylated polyester D-1 analyzed with GPC analysis.
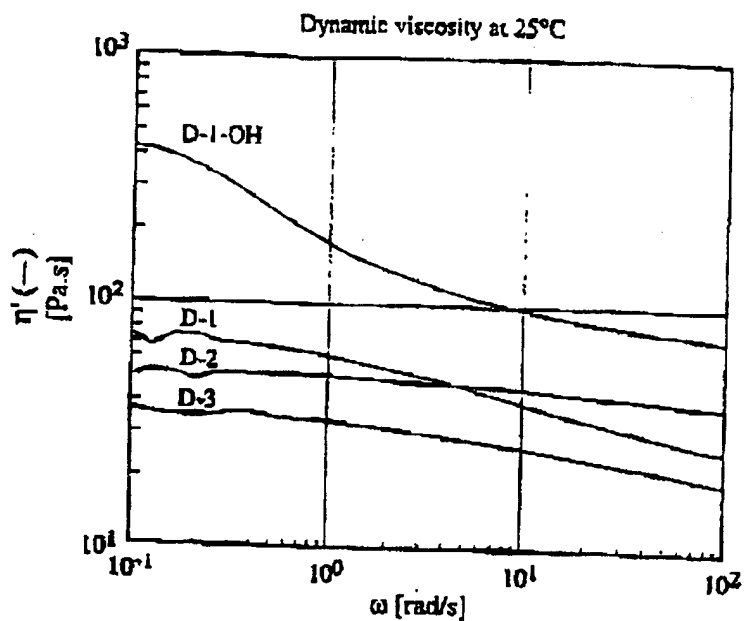

Figure 7   Dynamic viscosity of the hyperbranched (meth)acrylated polyesters.

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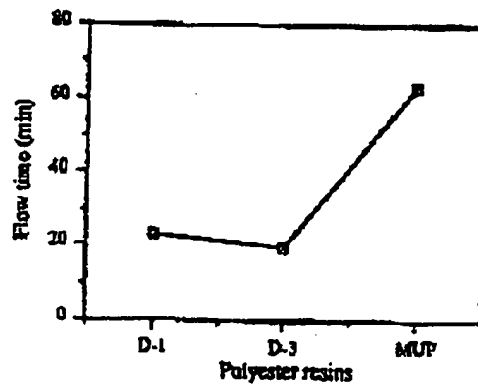
Figure 8 Flow time of hyperbranched polyesters and MUP using
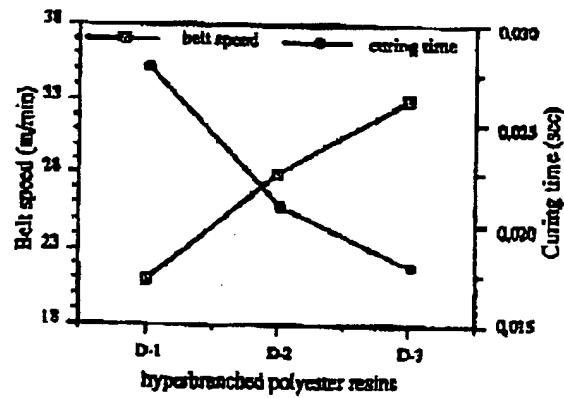   viscometric cup

Figure 9 Curing time and belt speed to tack-free state
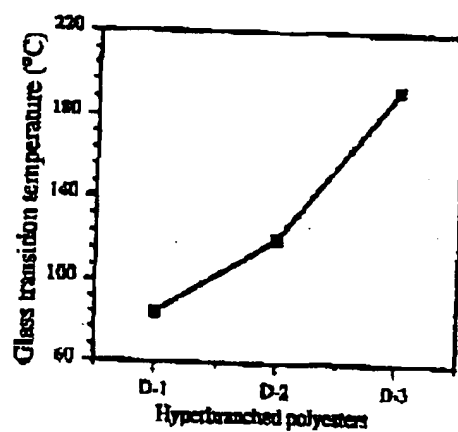   for UV cured polyester films

Figure 10 Glass transition temperatures of the cured hyperbranched polyesters.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 95/01013

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08G 63/20, C08G 63/78, C08J 3/28
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08G, C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

REGISTRY, CAPLUS, WPI, EPODOC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9318079 A1 (DSM N.V.), 16 Sept 1993 (16.09.93) --	1-29
A	WO 9317060 A1 (PERSTORP AB), 2 Sept 1993 (02.09.93) -- --------	1-29

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

* Special categories of cited documents:
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"E" earlier document but published on or after the international filing date
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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 December 1995	29 -12- 1995

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Form PCT/ISA/210 (second sheet) (July 1992)

International application No.
PCT/SE 95/01013

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		CA-A-	2117486	02/09/93
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		EP-A-	0630389	28/12/94
		JP-T-	6507512	25/08/94
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		SE-A-	9200564	15/03/93
		US-A-	5378886	03/01/95
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